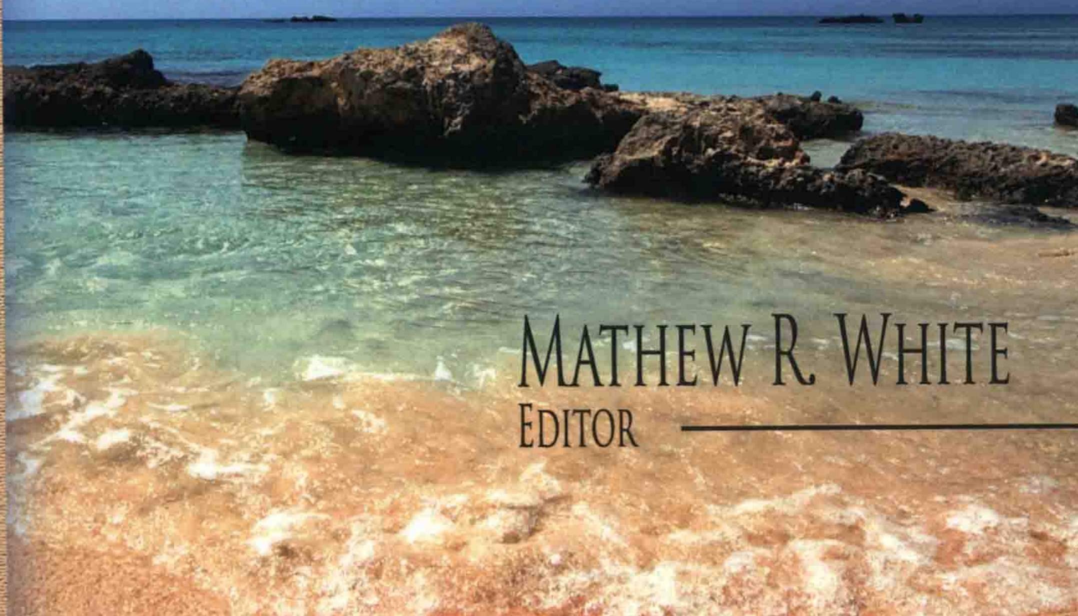
SEAWATER

GEOCHEMISTRY, COMPOSITION AND ENVIRONMENTAL IMPACTS



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OCEANOGRAPHY AND OCEAN ENGINEERING

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PREFACE

In this book, the authors present current research in the study of the geochemistry, composition and environmental impacts of seawater. Topics discussed include the impact of internal wave breaking on the ocean upper layer formation; trace elements in seawater in offshore oil production platform areas; self-purification of seawater; the Salton Sea megaport and seawater canal; and assessing the effect of nearshore currents over the SO2 absorption in Caribbean seawater.

Chapter 1 – The physical models of air-sea interaction mainly concentrated on the processes at the air-sea interface, surface waves, mixing within the ocean upper layer and the formation its hydro-physical structure including its lower boundary. The last one is relatively narrow seawater layer with the sharp seawater density increase with depth growth. This layer is often called the pycnocline. The dynamical and thermo-dynamical contribution of the pycnocline into the upper layer is routinely ignored because the very strong density stratification makes the lower boundary impermeable for dynamical and thermo-dynamical interactions with the main ocean body below the pycnocline. The exception is only internal waves propagating at the pycnocline. However the internal waves, like the surface waves, break at randomly distributed locations at the pycnocline generating turbulent patches which violate the pycnocline integrity and so its impermeability. The paper describes the effect of internal wave breaking turbulence on the structure of the hydro-physical and biogenic fields near the ocean surface. The exchange of turbulent energy, heat and biogenic salts between the ocean upper layer and the main body of the ocean below is caused through the random patches of active turbulence within zones of internal wave breaking. The variability of the upper layer temperature, concentration of biogenic salts and the turbulent energy is caused by the turbulence of the breaking zones, its variability and the breaking zones statistics. The turbulent horizontal diffusion of the ocean upper layer spread the non-uniformities of these fields into larger horizontal scales than the breaking zones scales. Estimates of the manifestation of the discussed mechanism are shown in the mean values and variances of the surface non-uniformities of the upper layer fields as well in their spectrums. The simple model examples of the field of internal wave breaking turbulence allow quantitative evaluation.

Chapter 2 – Produced water is the largest wastewater discharge in offshore oil, gas exploration and production processes. This water consists of formation water, the water naturally present in the reservoir, and floodwater injected into the formation. In general, in offshore operations, seawater is injected into the reservoir to maintain pressure in the formation for oil transportation. The produced water, that usually has a higher salt concentration than seawater, is separated from the oil and then discharged to the surface water. In this chapter, the characterization and evaluation of the trace elements and natural radionuclides in seawater in the *Bacia de Campos*, or Campos Basin, oil field region, in Brazil, is presented. In the present work, a representative region of oil-bearing activity in the *Bacia de Campos*, an oceanic region of the oil-field offshore platforms, represented by two fixed production platforms, was studied. The element and natural radionuclide content in dissolved and particulate produced water and seawater around the effluent discharge sites were studied. Six samples were collected at three different depths (surface (5 m), middle (45 m) and bottom (95 m)) in the oceanic region, with the sampling points allocated at 250 m, 500 m and 1000 m from the platforms, totaling 18 samples for each platform. The determination of V, Mn, Co, Ni, Cu, Zn, Cd and Pb was performed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) after solid phase extraction using online and offline montages. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) was used to determine Ba, Fe, Zn, Cd, Ni, Cr, Cu, Ag and Al in produced water and Ba in seawater. Uranium and molybdenum determinations were performed by ICP-MS with an ultrasonic nebulizer. Using one liter of produced water and twenty liters of seawater, after radiochemical separation, ^{210}Pb was determined by beta counting of ^{210}Bi, and ^{226}Ra and ^{228}Ra were determined by gross alpha and beta counting rate using a proportional 10-channel low-level proportional counter. The element concentrations in the effluents were, in general, compatible with the literature values and below the maximum acceptable values established by the Brazilian legislation. The measured activity concentrations ranged from 0.8 to 6.0 Bq L^{-1} for ^{226}Ra, from 0.7 to 8.2 Bq L^{-1}

for ^{228}Ra and from 0.04 to 1.9 Bq L^{-1} for ^{210}Pb, similar to values reported for other produced water around the world. A strong correlation between Ba and radium isotopes in produced water was observed. Element concentrations in seawater were similar at the two study sites. The values obtained for ^{226}Ra, ^{228}Ra and ^{210}Pb in seawater, were below 5 mBq L^{-1}. The results showed a high degree of dilution regarding the produced water samples for barium, radium isotopes, copper, cadmium, nickel and ^{210}Pb. In spite of the elevated element and natural radionuclide concentrations in the produced water, concentrations in the seawater from the vicinity of the effluent discharges were at the local background level.

Chapter 3 – The chapter deals with the development of radiochemoecological approach for evaluation of the maximum allowable input (MAI) of radioactive and toxic substances to marine environments, which combines assessment the capability of seawater for self-purification and toxicity of the pollutants. The net rate of self-purification is proposed to estimate using the time-series data on concentration in seawater of the fallout radionuclides, both well-soluble (^{137}Cs, ^{90}Sr) and particle-reactive ($^{239+240}Pu$). This provides opportunity for direct evaluation of the levels of maximum allowable discharge into marine environments of nuclear and non-nuclear pollutants; for differentiation between their effective and ecological half-lives; for assessment of capacity of aquatic ecosystems in respect of accumulation of contaminants. Quantification of toxicity may be expressed, in general, as the classic values of the maximum allowable concentrations (MAC), but there is an uncertainty regarding the applicability of many of national and international levels of MAC for environmental regulation of anthropogenic impact in marine ecosystems. This is particularly important for comparative assessment of the influence of nuclear and non-nuclear contaminants having different nature of biological effects and different dimensions. An approach for such the comparison is the evaluation of dosimetric equivalents (e.g., Grey-equivalent), which are used to compare the effects of ionizing radiation and other stressors in aquatic ecosystems. But this would require every time to carry out the parallel ecotoxicological and radioecological dose-effect experiments that is not always accessible. In order to overcome this difficulty, a dimensionless value expressed as a fraction of maximum ability of marine organisms for resistance to radiation or toxic exposures is discussed in this chapter based upon the early reported experiments on the effects of mercury and incorporated radionuclides on the marine unicellular algae. The developed MAI criterion may be useful tool for scientific justification of environmental control of pollution of seawater with the nuclear and non-nuclear substances at a common methodological basis. The chapter highlights also the questions related to environmental assessment of the state of marine ecosystems, which have been subjected to the structural changes due to anthropogenic influence, and their response through biogeochemical processes of compensatory homeostasis.

Chapter 4 – When the Saint Lawrence Seaway macro-project was completed in 1959, it opened a "Fourth Coast" for the USA. (Its East, Gulf and West Coasts were provided by Nature.) Excavation of a Canal connecting the Gulf of California, through Mexico to near the city of Mexicali and beyond to the USA would permit seawater flooding of the below-sea level Salton Sea, a briny, contaminated and smelly endorheic lake that is fast disappearing after its unnatural creation by man-made flash flooding in 1905-07. This chapter will fathom some mysteries of the Salton Sea, including some speculative informed comments that might seem like science-fiction or science faux. However, the author takes the discussion tack that a practical rendition of the possible future geographical facts for this inhabited and cultivated desert region of southern California and northern Mexico, namely "Alternative Zero", is more real-world than Peter D. Ward's *The Flooded Earth: Our Future in a World Without Ice Caps* (2010). Seawater can be a beneficent liquid, sometimes tranquil, soft and tractable. And, sometimes, it causes peril for humans, as well as economic losses. Not insignificantly, the San Andreas fault—the most well-known plate tectonic boundary in the world—parallels the easternmost edge of the existing Salton Sea; the bi-national seawater Canal and Megaport constructors, influenced by Walt Disney's "Imagineering" urban planning concepts, must make certain macro-project design allowances recognizing that geophysical reality. For Mexico, international commercial trade and tourism are the only industries that allow a net flow of wealth from richer to poorer nations. "Alternative Zero" has the potential to alter the climate of the Southwest as well as northern Mexico for the better.

Chapter 5 – An evaluation of the SO_2 absorption in Caribbean seawater is measured by the addition of sulphuric acid at different conditions. The Caribbean is characterized by two main seasons: dry and hurricane seasons such that the variations nearshore currents are present. The measurements were carried out in closed systems, using hypothetical effluents where the nearshore currents were simulated. The results indicated that the addition of sulphuric acid at high speed current reduces the buffer capacity quickly and its acidity can increase until 6.6.

CONTENTS

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Chapter 1

IMPACT OF INTERNAL WAVE BREAKING ON THE OCEAN UPPER LAYER FORMATION

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ABSTRACT

The physical models of air-sea interaction mainly concentrated on the processes at the air-sea interface, surface waves, mixing within the ocean upper layer and the formation its hydro-physical structure including its lower boundary. The last one is relatively narrow seawater layer with the sharp seawater density increase with depth growth. This layer is often called the pycnocline. The dynamical and thermo-dynamical contribution of the pycnocline into the upper layer is routinely ignored because the very strong density stratification makes the lower boundary impermeable for dynamical and thermo-dynamical interactions with the main ocean body below the pycnocline. The exception is only internal waves propagating at the pycnocline. However the internal waves, like the surface waves, break at randomly distributed locations at the pycnocline generating turbulent patches which violate the pycnocline integrity and so its impermeability. The paper describes the effect of internal wave breaking turbulence on the structure of the hydro-physical and biogenic fields near the ocean surface. The exchange of turbulent

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energy, heat and biogenic salts between the ocean upper layer and the main body of the ocean below is caused through the random patches of active turbulence within zones of internal wave breaking. The variability of the upper layer temperature, concentration of biogenic salts and the turbulent energy is caused by the turbulence of the breaking zones, its variability and the breaking zones statistics. The turbulent horizontal diffusion of the ocean upper layer spread the non-uniformities of these fields into larger horizontal scales than the breaking zones scales. Estimates of the manifestation of the discussed mechanism are shown in the mean values and variances of the surface non-uniformities of the upper layer fields as well in their spectrums. The simple model examples of the field of internal wave breaking turbulence allow quantitative evaluation.

1. Introduction: The Problem Formulation

Remote methods of measuring hydrophysical fields on the ocean surface have enjoyed extensive development during last three decades [Stewart, 1985; Martin, 2011]. This technique is in remote sensing applications since 1970's to record surface elevations [Zagorodnikov, 1978; Glazman, 1991], and surface temperature [Galaziy, Shifrin and Sherstyankin, 1979; Minnett, 1990; Schluessel and et al., 1990], wind above the ocean surface [Kelly and Caruso, 1990; Lalbeharry, Khandekar, Peteherych,1990; Willard and Pierson, 1990] and biological surface fields [Dickey, 1991; Hood and et al., 1990]. The remote methods are of fundamental interest to investigation of the ocean using artificial earth satellites [Fedorov and Sklyarov, 1980; Stewart, 1985; Dickey, 1991; Wahl and Simpson, 1990; Martin, 2011].

Among the diverse processes responsible for forming surface non-uniformities in hydrophysical fields, internal waves, which are encountered everywhere in the ocean, play an important role. They influence surface temperature, and they change the nature of surface disturbance, forming slicks--areas of smoothing of small-scale wave components [Fairbridge, 1966; Steele, Thorpe and Turekian, 2009].

The action of internal waves upon surface characteristics of hydrophysical fields may manifest itself in two ways. First, the internal wave field induces a field of surface movements which can lead to formation of surface non-uniformities in hydrophysical fields of the scale of internal waves [Monin and Piterbarg, 1977; Fedorov, 1981]. Second, internal waves affect the turbulence of the ocean upper quasi-uniform layer. The turbulence is responsible for vertical mixing in the upper layer, and in turn it has a strong influence upon

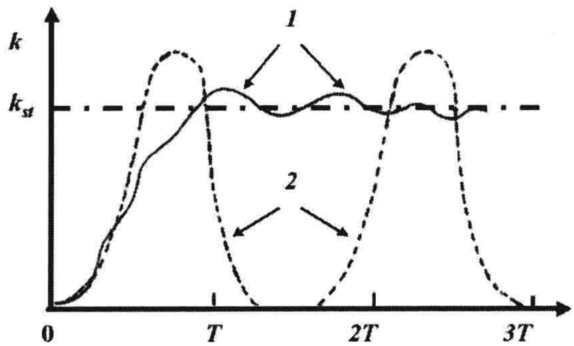

Figure 1. An example of the internal wave effect on the turbulent kinetic energy k (TKE) in a current of stably stratified fluid [Ivanov et al., 1982]; 1 - TKE modulated by the internal wave with the period T near a steady state k_{st} induced by the mean shear, 2 - local generation of turbulence by the internal wave shear.

surface and internal waves [Hasselmann, 1966; Fedorov and Sklyarov, 1980; Ivanov et al., 1982; Benilov, 2013]. The effect of internal waves on upper layer turbulence manifests itself in the form of modulation of the turbulence statistical characteristics by internal waves [Ostrovskiy and Soustova, 1977; Ivanov et al., 1982; Ostrovskiy and Piterbarg, 1997], and as an effect of turbulence, which is produced by the internal waves breaking, upon the upper turbulent layer [Barenblatt and Benilov, 1982; Benilov 1984, 1986; Benilov and Gavrilin, 1988; Bock et al., 1990; Moum et al., 1990; Wijesekera and Willon, 1990]. Figure 1 shows an example calculated by Ivanov et al.[1982] that demonstrates the internal waves effect on turbulence. In the case of weak interaction (line 1) the TKE (turbulent kinetic energy) is modulated by the shear of internal wave with the period T near a steady state k_{st} induced by the shear of mean current and the oscillations of TKE have the period of the internal wave. The events of local generation of turbulence by the shear of internal wave are illustrated by line 2.

The effect of turbulence on surface waves differs fundamentally for waves of scale ℓ greater than 10 cm (gravity waves), and for waves of scale ℓ less than or equal to 10 cm (ripples). In the first case ($\ell > 10$ cm) the propagation of surface gravity waves obeys well to the potential theory. The upper layer turbulence occurs due to the energy flux j from the potential wave motion into the vortex turbulent motion. This energy flux transfers the kinetic energy E_φ of the wave field into the turbulent kinetic energy [Benilov, 1973; Benilov and Ly, 2002] in the direction opposite to the gradient of E_φ that is:

$$\boldsymbol{j} = -\nu_T \boldsymbol{grad} E_\varphi \quad (1)$$

where ν_T is the coefficient of turbulent exchange of wave energy E_φ. This coefficient may be assumed to be proportional to the coefficients of exchange of momentum and turbulent energy. The wave energy spreads throughout the entire upper layer by the energy flux ***j***. This is what leads to smoothing the surface waves with scale $\ell > 10$ cm. Also, the contribution of the internal waves should be taken for consideration. At the bottom of the upper mixed layer there are internal waves, which propagate within the density discontinuity layer and some time break, and then localized turbulent zones occur in the vicinity of the lower boundary of the upper layer. These turbulent zones may widen, raising the intensity of turbulence in the upper layer. It means that the upper layer may have an additional influx of turbulent energy from the area of the internal wave breaking. As a result of this, the coefficient of turbulent diffusivity ν_T increases, and because ***grad*** E_φ is not small near the free surface, the turbulent flux of wave energy increases. Hence, it follows that areas of smoothing on the free surface will appear over areas of breaking internal waves. In the case of low turbulence intensities within breaking zones the turbulent energy flux will have the reverse direction, i.e. the upper layer turbulence will feed the turbulence of the breaking zone. As a consequence the smoothing of the ocean surface is expected in the areas unperturbed by the internal wave breaking, since the level of unperturbed turbulence would turn out to be higher than the level of perturbed turbulence.

Fluctuations of the ocean surface having a scale range of $\ell \leq 10$ cm (ripples) are different in nature. A detailed analysis of experimental data on wind waves carried out by Zaslavskiy [1981] and Zaslavskiy and Leykin [1981] shows significant deviations of the measurements from the conclusion of linear potential theory concerned with this range of scales. Yefimov and Khristoforov [1971] noted that these differences indicate that the velocity field is determined to a significant extent by turbulent motion in this range of scales. The study [Zaslavskiy, 1981; Zaslavskiy and Leykin, 1981] of the properties of the empirical dispersion relation of small-scale waves obtained by processing the observation data confirms the conclusions [Yefimov and Khristoforov, 1971]. It follows from the empirical fact that the scattering magnitude $\Delta\omega$ of the empirical dispersion relation is about the same order of magnitude as the frequency ω itself. As one can see, the single-valued connection between both the frequency ω and the wave vector **k** does not take place here, and it is one of the principal indicators of the turbulent nature of fluid motions. The random vortex nature of surface turbulence may be a product of irregularities of tangent stresses generated by the atmospheric turbulent boundary layer on the ocean surface and, also, the breaking of surface waves. According to the data [Kuznetsov, 1978], the variations of the friction velocity v_* of the atmospheric boundary layer correlate well with the r.m.s. of the sea surface elevations measured in the frequency range 1-10 Hz.

Relying on the experimental facts presented above, we can identify small-scale fluctuations in the ocean surface with ordinary turbulence, which may be described, for instance, within the framework of the modern semi-empirical turbulence theory. What are the consequences of this assumption for the ocean surface? Modulation of the turbulence of the upper layer by internal waves leads to the appearance of alternating spots or slicks. The scale of this phenomenon will be equivalent to that of internal waves. Non-uniformities caused by the breaking of internal waves are superimposed over this pattern. For the range of scales of surface fluctuations under examination here ($\ell \leq 10$ cm), the effects will be directly opposite to what was noted in the case of fluctuations with scale $\ell \geq 10$ cm. When the intensity of upper layer turbulence is increased by an influx of turbulent energy from zones of the internal wave breaking, the surface would be less smooth than in areas which are not perturbed by breaking waves, while on the other hand the surface would be smoother wherever upper layer turbulence feeds the turbulence of the breaking zone and wherever a drop in the level of turbulence within this layer exists. In the case where the turbulence of the center of the breaking zone significantly exceeds the turbulence in the upper layer, one breaking zone projects itself to the surface in the form of two smoothing spots, which merge into one as the turbulence of the breaking zone drops with time. This double-relationship pattern stems from nonuniformities in the distribution of turbulence within the breaking zone itself - the turbulent intensity is high in its center, and low on the periphery. This paper is devoted to the discussion of the latter mechanism.

To reach the posed objective we need to build a model satisfactorily describing formation of the upper mixed layer, the equilibrium characteristics of which are determined by atmospheric influences upon the surface and by background stratification outside the layer. The model must describe interaction of upper layer turbulence with abyssal turbulence generated by the breaking of internal waves and by other mechanisms. It seems as if the theory of this phenomenon could be derived using the traditional methods of the semi- empirical theory of turbulence. Below we shall use the approaches developed in [Barenblatt and Benilov, 1982; Benilov 1984, 1986] to fulfill the listed requirements.

2. The Upper Turbulent Layer

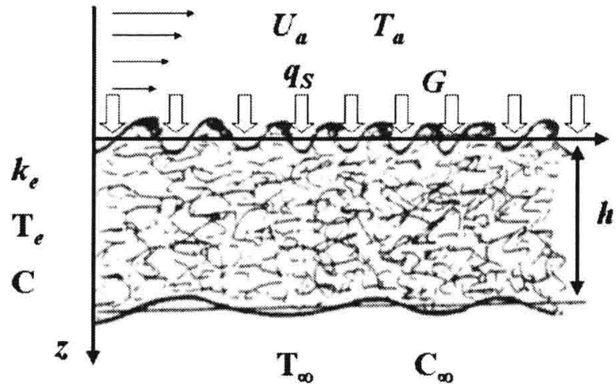

Figure 2. The oceanic turbulent upper layer in thermo – dynamic equilibrium with the atmospheric boundary layer without the internal wave breaking turbulence; U_a is the wind velocity; T_a is the air temperature; q_s is the energy flux; G is the heat flux; h is the upper layer thickness; k_e, T_e, C are the TKE , the temperature and the biogenic salts (mineral nutrition) concentration of the upper layer; T_∞, C_∞ are the temperature and the biogenic salts (mineral nutrition) concentration of the main water body of the ocean.

We will examine, as a model of the upper turbulent layer of the ocean, a liquid occupying a region of space $z \geq 0$ (Figure 2, axis z is directed vertically downward). Density stratification is determined by vertical change in temperature, T. The analysis is conducted on the basis of an approximation of the upper quasi-uniform layer continually filled with turbulence and separated from the non turbulent region by a sharp boundary [Barenblatt, 1977] (mixing ceases where turbulent kinetic energy, k, reduces to zero). Thus it is assumed that the upper mixed layer occupies the layer of the thickness h ($h \geq z \geq 0$), the temperature in the upper layer does not depend on the vertical coordinate z, but that it does depend on time t: $T = T_s(t)$ (the traditional approximation in models of the upper quasi-uniform layer [Kraus and Businger, 1995]), and that beyond its lower boundary the temperature is constant and equal to $T = T_\infty = const.$ The state of the atmosphere over the ocean is characterized by wind velocity U_a and temperature T_a at a standard measuring height $z = z_a < 0$. The wind above the free surface of the ocean generates the wind surface waves. The surface wave breaking produces fluxes of turbulent energy q_s and as well as momentum [Benilov, 2013] that maintains the turbulence of the upper layer (Figure 2.). According to the estimates carried out in [Longuet-Higgens, 1969; Benilov, 1973; Benilov and Ly, 2002] these fluxes are associated with the phase velocity C_0 of the spectral maximum of wind waves. The energy flux is given by the expression $q_s \approx 5\times10^{-8}C_0^3$. In the case of developed waves the phase velocity C_0 of the spectral maximum satisfies the approximate equality $C_0 \approx U_a$ [Kitaygorodskiy, 1970]. Then, in the case of developed waves, the energy flux q_s becomes

$$q_s \approx 5\times10^{-8}U_a^3, \tag{2}$$

that corresponds to the steady situation depicted in the diagram in Figure 2.

Heat flux G from the atmosphere to the upper layer may be represented in the form

$$G = C_T\rho_a c_{pa} U_a (T_a - T_s), \tag{3}$$

where $C_T \approx 10^{-3}$ is the heat transfer coefficient [Kitaygorodskiy, 1970; Kanta and Clayson, 2000], ρ_a is the air density, and c_{pa} is the specific heat of air. In the absence of breaking of internal waves, which in this approximation are excited by turbulence of the upper layer at its lower boundary $z = h$, the atmosphere and the upper layer are in thermal and dynamic equilibrium: the energy flux from the surface waves is completely expended by dissipation and work against the buoyancy forces.

When the atmosphere and upper layer are in thermal equilibrium, $G = 0$ and $T_a = T_s$. Thus the equilibrium of the upper layer in steady state is determined completely by three constant dimensional parameters q_s, $\delta T = T_a - T_{\infty}$, and the buoyancy parameter, $\beta = g\alpha$, where α is the coefficient of thermal expansion of liquid and g is the acceleration due to gravity. Therefore:

$$[q_s] = L^3\tau^{-3};\ [\delta T] = \theta;\ [\beta] = L\tau^{-2}\theta^{-1} \tag{4}$$

where L is the length dimension, τ is the time dimension, θ is the temperature dimension.

The effect of the mean velocity shear is not accounted in this approach because, by the initial assumption, the energy flux from the surface waves is